Speeding up the transition to greener surfactants

The green trend continues to gain momentum and increasingly consumers base purchasing decisions on perceived health and environmental benefits. This is particularly true in the cosmetic and personal care space where the number of products carrying green claims are on the rise.

The Problem

One key class of ingredients in cosmetics and personal care products are surfactants. Used to create emulsions and microemulsions, surfactants help the water and "oil" components to hold together in stable formulations. There's clearly a desire to replace conventional surfactants with naturally derived, sustainably sourced or biodegradable alternatives but for the cosmetic scientist the challenge of reducing this switch to practice is a tough one.

There are very few ways for determining which surfactant is the best green replacement, especially when working with microemulsions. Trial and error takes time, eating into a company's competitive edge so it is clear a framework for rational formulation design would be beneficial. Outlined here is a real alterative to the limited Hydrophilic-Lipophilic Balance (HLB) approach.

HLD-NAC Theory

A highly promising approach for identifying key parameters is the Hydrophilic Lipophilic Difference (HLD) - Net Average Curvature (NAC) methodology of Professor Edgar Acosta from the University of Toronto, built on the HLD concept developed by Aubry, Salager, Sabbattini and others. HLD theory is well-established in the oil industry but little-known for cosmetics.

The HLD uses a simple equation based on salt concentration, oil "number" and the surfactant characteristic curvature (Cc) which identifies the region in surfactant space where the surfactant is most useful. A simple equation determines how close a mixture is to the "optimal formulation" where the smallest amount of surfactant gives the largest amount of (micro) emulsification.

If the Cc of the surfactant is far from this optimum the emulsion is inefficient /poor. If the Cc is slightly lower than optimum an efficient type I oil-in-water (o/w) emulsion is produced and if it is slightly higher an efficient type II water-in-oil (w/o) emulsion is formed.

Importantly, the Cc of a mixture of surfactants is the weighted average of the two. Optimal surfactant mixtures with the desired Cc can be created from combinations of surfactants. Surfactant mixtures are common in cosmetic formulation and HLD theory, uniquely, makes it possible to find optimal mixtures efficiently.

Determining Cc values

The Cc values are known only for a few dozen surfactants. Catalogues of green surfactants contain hundreds of possible choices but provide no guiding Cc values.

Measuring Cc is not very difficult. Take, for example, 8 tubes containing measured amounts of water, surfactant, salt and 8 different oils spanning the appropriate HLD range. Phase transition from w/o to o/w via a type III bi-continuous oil and water emulsion determines the optimal point from which a Cc value can be calculated (see Figure 1).

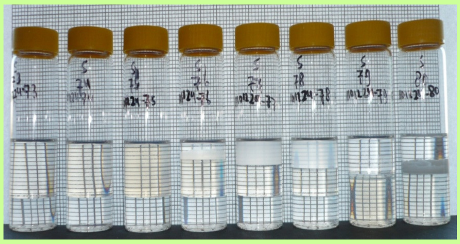

Figure 1 — Transition from w/o (type II) microemulsions on the left to o/w (type I) microemulsions on the right allows determination of a surfactant's Cc value. The transition (type III) can be seen in the 5th tube from the left. Phase volumes provide extra information, covered by the NAC part of HLD-NAC theory.

Doing this process for multiple surfactants is tedious, time consuming and resource intensive. We therefore developed a quick, efficient and accurate method to determine Cc values of

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multiple surfactants using a high throughout screening method.

High throughput

Specialised high throughput equipment, such as the Chemspeed Formax, can be utilised to greatly increase processing power. Robotic determination of Cc values can be carried out 4 times faster than by traditional long-hand phase scans, significantly decreasing the required man power and greatly improving accuracy. This is the first time high throughput screening and HLD-NAC have been brought together.

Figure 2 – Chemspeed Formax at VLCI, Amsterdam

Cc values of Green Surfactants

A number of the key surfactant suppliers generously provided a range of green surfactants.

They were chosen to cover a large range from hydrophilic to hydrophobic, ionic and non-ionic, ethoxylated and non-ethoxylated, sugar-based, natural extracts etc. Of the 22 surfactants tested Cc values were determined for 13 (see Table 1).

For the remaining 9, definite values could not be defined within the bounds of this project but minimum or maximum ranges were determined. In general it's desirable to formulate with surfactants with Cc values from -2.5 to 2.5. Within this range surfactants match well to typical oils and formulation conditions. Outside of this range surfactants are more difficult to match and therefore not a first choice as a principle ingredient.

Building formulations based on Cc values: the benefits

Using the measured Cc values makes it much easier to get reasonable first approximations to good formulations.

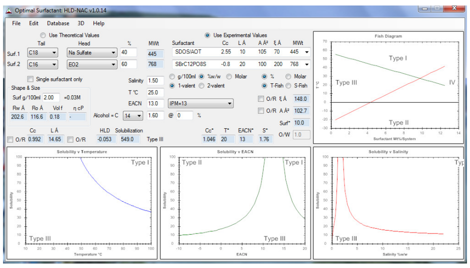

Figure 3 – the free Optimal Surfactant software used for formulation work.

Although the HLD-NAC equations are simple, help from software (and the database of Cc values inside it) makes it even easier to use and to understand how to adjust formulations to improve them further. This system provides:

- Improved prediction of surfactant performance in a given formulation,
- Reduced formulation development time, cost and resource,
- Easier selection of appropriate green surfactant alternatives,
- Elimination of surfactant adjustment with alcohols, the fine tuning of formulations with mixtures of surfactants is possible by calculation of combined Cc value.

As a result of this project Syntopix Group plc have identified two new green surfactants for incorporate into novel oral care microemulsions.

The future

All Cc values from the project have been placed in the public domain. In particular the Optimal Surfactant software (www.stevenabbott.co.uk/HLD-NAC.html) has these values included in its database allowing users to find their own surfactant formulations. The team have also provided an Instant Guide to HLD-NAC. It is hoped this project will encourage surfactant suppliers to measure and provide Cc values to aid their customers in formulation design.

Green Surfactant Cc Values

Name	Cc
C13C15 oxo alcohol & approx 7 moles of EO	-0.7
Yucca saponins	<-2.4
Sodium cocoyl sarcosinate	<-2.8
Sodium lauroyl sarcosinate	-4.2
Isotridecyl alcohol 8 mole ethoxylate	-0.1
Polysorbate 20 (POE sorbitan dodecanoate)	-7.9
Polysorbate 80 (POE sorbitan 9-octadecanoate)	-3.7
Sorbitan monolaurate	3.5
Soy lecithin	4
Sodium dihexyl sulfosuccinate	-0.9
Octyldecyl glucoside (Guerbet-type)	<-2.4
Laureth-4	>1.5
Protodioscin beta-diglucorhamnoside)	< -1
Sucrose palmitate	-0.8
Sucrose distearate	4
Fatty alcohol C12-C18 with approx 14 moles EO	-2.9
PEG-20 glyceryl stearate	<-2.4
Octyldodecanol (C20-Guerbet alcohol)	>4
Laureth-7-citrate (citric acid ester of lauryl E7)	> -0.75
Sodium stearoyl glutamate	-5.0
Fatty alcohol C8 with approx 4 moles EO	0.25
Fatty alcohol C12-C14 with approx 9.5 moles EO	<-2.4

Table 1 - Measured Cc values. Please note that values for surfactants can be source dependent. Values can typically range over +/- 0.2 depending on control of chain length, branching, residual alcohols, salts etc.

The 30 day Formulation Challenge Project

Supported by Intelligent Formulation Ltd this was a 30 day challenge project aimed at stimulating innovation in the formulation space. Dr. Gavin Donoghue and Sarah Gregory from Syntopix Group plc identified a need for rational microemulsion formulation design. The challenge brought together two surfactant experts, Prof Edgar Acosta at the University of Toronto (expert in HLD-NAC theory) and Dr Ian Callaghan an independent consultant. Prof Steven Abbott of the University of Leeds and a consultant to Syntopix provided the Optimal Surfactant software and acted as project leader. Sander Van Loon led the VLCI team running the high throughput scans. The team thanks David Calvert of Intelligent Formulation for overall coordination of the project. For further information:

www.intelligentformulation.org www.stevenabbott.co.uk/HLD-NAC.html http://vlci.biz/ www.syntopix.com